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(for Harry Cikanek)

Update on N_2O_4 Molecular Sieving with 3A Material at NASA/KSC[1]

Chuck Davis
NASA, Kennedy Space Center, Florida
And
Claudia Dorn
Wyle/United Paradyne Corporation,
Kennedy Space Center, Florida

ABSTRACT

During its operational life, the Shuttle Program has experienced numerous failures in the Nitrogen Tetroxide (N_2O_4) portion of Reaction Control System (RCS), many of which were attributed to iron-nitrate contamination. Since the mid-1980's, N_2O_4 has been processed through a molecular sieve at the N_2O_4 manufacturer's facility which results in an iron content typically less than 0.5 parts-per-million-by-weight (ppmw). In February 1995, a Tiger Team was formed to attempt to resolve the iron nitrate problem. Eighteen specific actions were recommended as possibly reducing system failures. Those recommended actions include additional N2O4 molecular sieving at the Shuttle launch site.

Testing at NASA White Sands Test Facility (WSTF) determined an alternative molecular sieve material could also reduce the water-equivalent content (free water and HNO_3) and thereby further reduce the natural production of iron nitrate in N_2O_4 while stored in iron-alloy storage tanks. Since April'96, NASA Kennedy Space Center (KSC) has been processing N_2O_4 through the alternative molecular sieve material prior to delivery to Shuttle launch pad N_2O_4 storage tanks. A new, much larger capacity molecular sieve unit has also been used. This paper will evaluate the effectiveness of N_2O_4 molecular sieving on a large-scale basis and attempt to determine if the resultant lower-iron and lower-water content N_2O_4 maintains this new purity level in pad storage tanks and shuttle flight systems.

BACKGROUND

This paper is a continuation of a 1998 JANNAF Propellant Development Characterization Subcommittee paper entitled, "N_2O_4 Molecular Sieving With 3A Material at NASA/KSC." Therefore, the reader is referenced to this previous paper for the detailed background of this project. To summarize, over eighty N_2O_4 RCS valves have failed in either ground processing or in-flight during the history of the program. Numerous quick-disconnect devices have also failed. Iron nitrate is a long-recognized contaminant and was implicated in many of these failures. In February 1995, NASA Johnson Space Center initiated a program-wide Tiger Team to investigate RCS valve failures. One area identified was to improve the quality of the N_2O_4 being loaded into Shuttle systems. NASA WSTF had identified an alternative molecular sieve material "Molsiev® Adsorbent Type-3A" which also reduced water-equivalent[2] content in addition to reducing iron in N_2O_4. KSC changed its mole sieve to the 3A material in April 1996. Since then, delivery tankers are transferred through the KSC-molecular sieve into a KSC-based tanker. The KSC tankers are later delivered to either Launch Complex 39A or B N_2O_4 pad storage tanks, referred to as Ready Storage Vessels (RSV). All components are constructed primarily of 304L stainless steel and have been in service for several years. Therefore, any iron that now leaches from these systems into the N_2O_4, should be from the natural long-term corrosion-rate of the systems. Photo 1 shows the LC 39A N_2O_4 RSV with the cross-country piping to the pad tower. Until recently, KSC had used a small unit, Iron Removal unit 3 (IR3) for its molecular sieving operations. A much larger capacity unit, Iron Removal unit 4 (IR4), was activated in September 1999. Photos 2 and 3 are of the two units.

[1] The work described in this paper was carried out at NASA, KSC, with in-house resources.
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[2] Water does not readily exist as H_2O in N_2O_4. Rather, the water converts the N_2O_4 into nitric acid (HNO_3) and nitric oxide (NO). Hence, the term "water equivalent" actually represents the sum of free water (usually none) and nitric acid contained within N_2O_4.

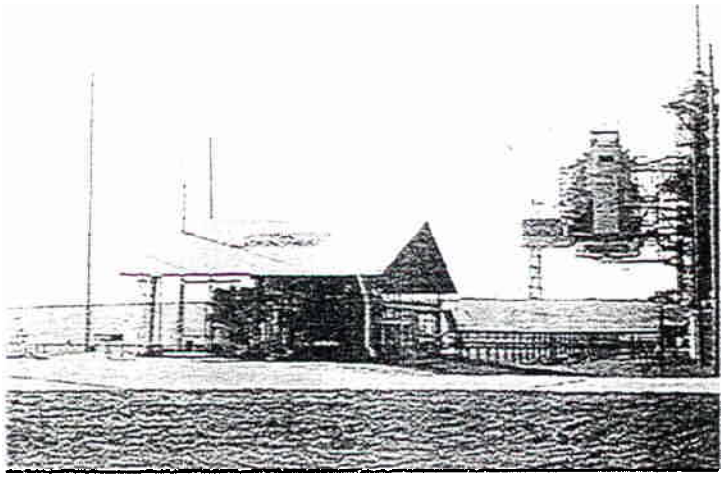


Photo 1: LC 39A N2O4 RSV. LC 39B RSV is nearly identical.

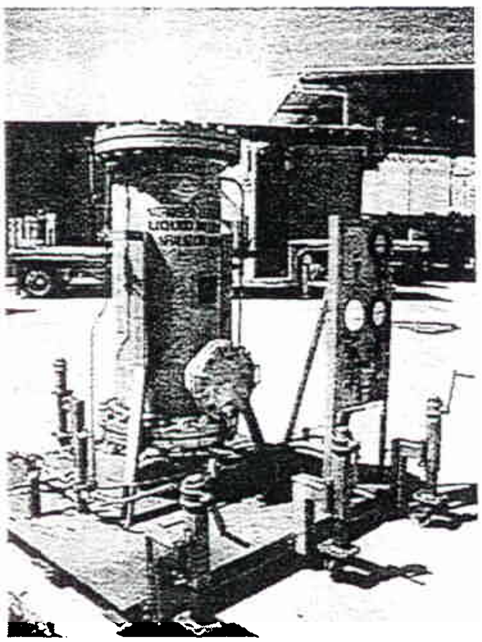


Photo 2: IR-3

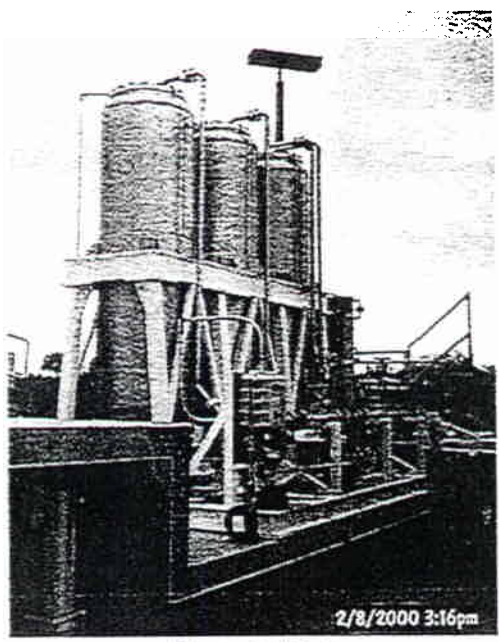


Photo 3: IR-4

Table 1 compares the various N_2O_4 specifications referenced herein. The delivery tankers generally conform to the "Procured" specification. "Delivered" generally refers to "at the interface" between the flight hardware and ground support equipment and is representative of an RSV. The Tiger Team proposal would replace current SE-S-0073 requirements.

Table 1: Comparison of Current Shuttle N2O4 Specifications

CHARACTERISTIC	PROCURED	DELIVERED	TIGER TEAM PROPOSED
SPECIFICATION:	**MIL-PRF-26539E**	**SE-S-0073, Table 6.3-10**	**Reference 2**
NO content	2.5% (min) to 3.0% by wt (max)	1.5% (min) to 3.0% by wt (max)	2.5% (min) to 3.0% by wt (max)
Iron	0.5 ppmw (max)	1.0 ppmw (max)	0.1 ppmw (max)
Water Equivalent (H_2O + HNO_3)	0.17% by wt (max)	0.20% by wt (max)	0.05 % by wt (max)

There appears to be no definitive data indicating a minimum level in which iron nitrate and water equivalent will cause component problems. Therefore, KSC recommended if the N_2O_4 specification was changed, then the change should be based on operational molecular sieving results. Therefore, the data summarized in this paper should indicate achievable purity levels to which SE-S-0073 could be changed with a reasonable expectation of meeting such requirements in an operational environment.

EXPERIMENTAL APPROACH

Additional N_2O_4 sample analysis data was added to the original paper's data from all N_2O_4 samples taken in support of the Shuttle Program from January 1998 through December 1999 (e.g. flight tanks, ground storage tanks, and delivery tankers). Thus, four years worth of data are included here. To determine the 3A molecular sieve materials' effectiveness, each delivery tanker was sampled prior to off-loading through the molecular sieve. The "receiving" KSC tanker was sampled with the before-and-after-molecular-sieving analyses compared to determine mole-sieving effectiveness. The Cape Canaveral Air Force Station Aerospace Fuels Laboratory analyzes tanker samples. Wiltech, the KSC laboratory, provides routine N_2O_4 analysis of LC39 RSVs and Shuttle flight tanks. Both labs use similar test methods for iron, water equivalent, and NO determinations (see MIL-PRF-26539E for methods). This paper uses data from day-to-day propellant operations and analysis methods at a space-launch site, not a research facility. Therefore, no attempt was made to create control standards beyond standard operating procedures.

IR4 START-UP AND INITIAL OPERATION

The initial operation of IR4 was conducted in October 1999. A 500-gallon capacity Generic Propellant Transfer Unit (GPTU) was used instead of tankers so flow rate data could be collected using the GPTUs' load cells. The towers were monitored for possible heating when first wetted with N_2O_4 but no temperature increase was noted. The first run indicated a flow rate of 15.6 gpm. Throttling the flow-control valve did cause the pump to shutdown due to low-flow as intended. Additional pump runs will be necessary to optimize the position of the manual flow control valve and to evaluate pump operation.

Each operation took one day. Although IR4's pump allows for faster flow, the overall process is not necessarily faster than using IR3. Additional time is required for venting and pressure loading the initial 660 gallons needed to fill the towers before pumping can commence. This took as much as 1-½ hours. Then pump flow can proceed for about 1-½ hours to nearly-empty the tanker. After pump shutdown, residual N_2O_4 was pressure off-loaded from the supply vessel, followed by draining of residual N_2O_4 from the three towers, which can take another 3 hours. The time consuming part is making connections to various drain points, pressurizing, draining, and purging. If the system were operated in a circulation mode, such as at the Shuttle pad RSV, IR4 should be considerably faster than IR3 due to the faster flow-rate through IR4. Conducting a RSV purification operation was a primary design consideration for IR4.

Analyses for media breakdown products such as aluminum, silica, magnesium, sodium, chromium, potassium, etc. show concentrations <0.01 ppmw both before and after an operation. This is consistent with samples taken in 1998 when IR3 was changed over to the 3A media. Particles were present in much greater quantity, though not enough to fail specification limits, in all size ranges (5-10/10-25/25-50/50-100/>100 micron, & metallics >50 micron) from IR4 as compared to IR3. IR4's outlet filters (25 micron) are not nearly as fine as the IR3 outlet filter (0.2-micron). IR4 throughput at the time of this writing totals 6,909 gallons of N_2O_4 with removal of 68.5 pounds of water.

As IR4 experiences more run time, periodic samples will be taken from each tower to see how much of a difference there is in the performance of each tower. Tower monitoring and subsequent "regeneration" or "drying" of the media is as yet to be developed. The thought is tower #1 will be the first to become saturated with water. Thus, we expect tower #1 will require regeneration more often than the other two towers. The current planning is to not allow all three towers to become completely exhausted, but rather regenerate tower #1 alone with a hot nitrogen purge. Several key questions are yet to be answered. Will the monitoring be able to detect "exhaustion"? How will the drying process be conducted? How well will the drying process work, and at what point is drying ineffective and media replacement required? Towers #2 and #3 regeneration frequency will be determined after resolving tower #1 issues.

Table 2: COMPARISON OF IR3 TO IR4 as of 10/99

Parameter	IR3	IR4 (on the trailer)	IR4 Design Parameter
Height	6.3 ft	14.4 ft	11.9 ft
Width	6.6 ft	10 ft	7.9 ft
Length	9.6 ft	34 ft	10 ft
Weight (total system)	4340 pounds	~25,000 pounds maximum when loaded	
Media Quantity	300 lb.	3,000 lb.	3,000 lb.
Water Removal Capacity	52 lb. water	600 lb. water	600 lb. water
Typical Throughput to Deplete Media	9,038 gallons	TBD, currently at 6,906 gallons	9,300 gallons
Ave. Concentration of Water-Equiv. in Effluent	0.06 wt.%	0.01 wt.%	<0.02 wt.%
Average Concentration of Iron in Effluent Product	<0.1 ppmw (by AA-method)	0.02 ppmw (by ICP-method)	<0.05 ppmw
Typical Lose in Nitric Oxide Concentration	0.1- to 0.2 wt.%	0.1- to 0.2 wt.%, evaluation ongoing	-
Average Flow Rate	5-8 gpm	10.7 - 25 gpm	10.7-25 gpm
Filter Capabilities	0.2 micron	Particles in all size ranges	10 micron absolute 25 micron maximum
Max. Allowable Working Pressure	150 psig	230 psig	230 psig
Max. Operating Pressure	50 psig	165 psig	165 psig
Typical Run Time To Process a 2400 Gallon Tanker	9 hr.	Currently takes up to 9 hr.	No data - assumed to be well under 9 hr.
System Liquid Volume	81 gallons	~660 gallons	-
Residual Product Drain	1-2 gallons	~ 30 gallons	-

KSC Molecular Sieving Effectiveness

The "old" molecular sieve unit, IR3[3], contains 300 pounds of media and typically processes N_2O_4 at 5-8 gallons per minute (gpm). Historical operating data shows actual water-adsorption capacity to be approximately 52 pounds with a throughput of approximately 9,000 gallons of N_2O_4. Four separate batches of oxidizer were processed through IR3 in 1997 & 1998. The average change in water-equivalent content was 0.05 wt.%, with water-equivalent levels as low as 0.06-wt.% being achieved. During these operations, the nitric oxide content would typically be reduced by 0.2 wt.%. A typical iron (as iron nitrate) reduction was 0.2 ppmw with the final concentration being less than 0.1 ppmw.

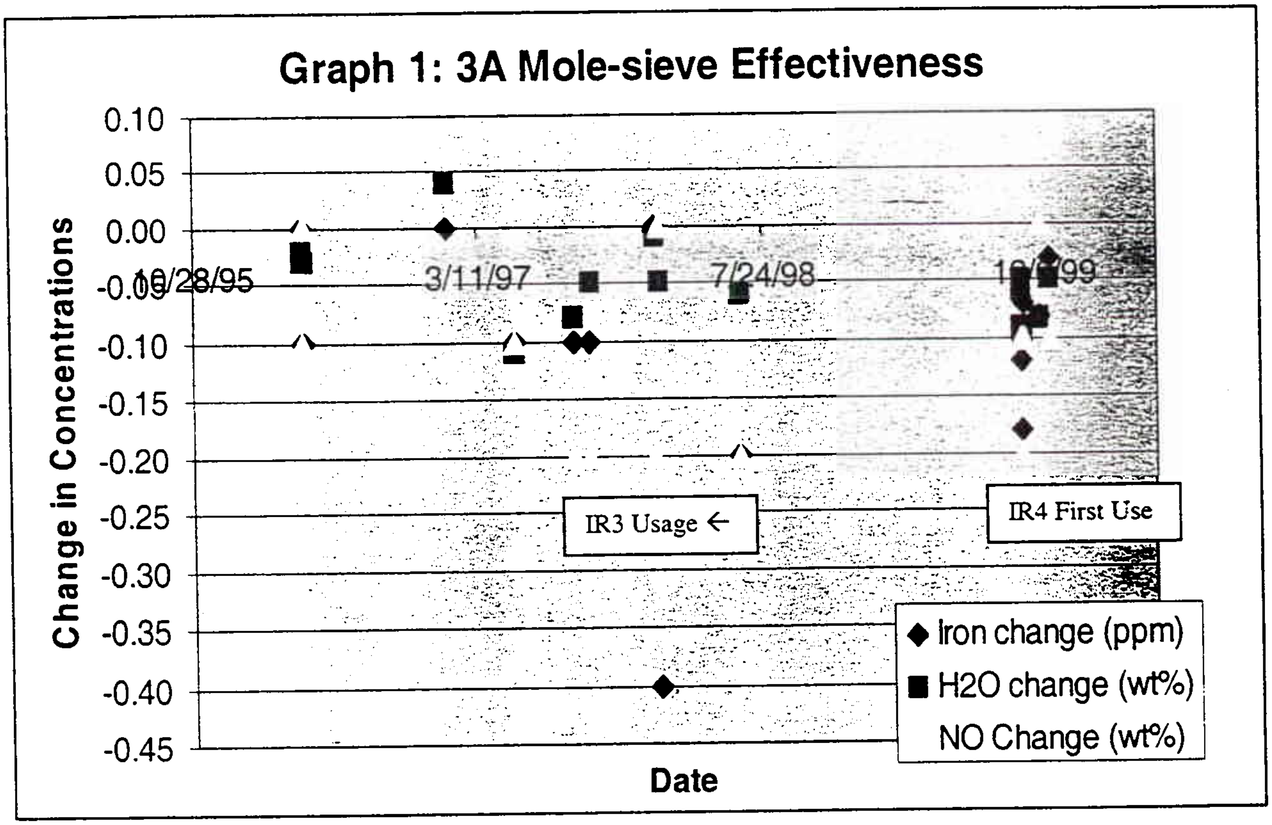
A typical IR3 operation consists of connecting hoses, filling the tower with oxidizer while venting to ensure it is packed, flow, purging residual liquid out of the system, and disconnecting the hoses. Processing 2300 gallons in a tanker takes about 9 hours. IR3 holds approximately 81 gallons of N_2O_4.

The "new" molecular sieve unit, IR4, was first activated in October 1999. Although this unit contains a pump, the system needs to be filled with liquid using a pressurant gas prior to pump activation. Therefore, the operational steps for starting operations with IR4 are very similar to IR3: connect hoses, fill towers (three each), fill filters, flow (with pump at 15- to 25 gpm), pressure-purge residual liquid out of the system, and lastly, disconnect hoses. Due to its numerous valves, gauges, pressure- and flow-switches, and many piping components, IR4 is more complex a system to operate than IR3. Unfortunately, it also has many more components that can break down.

[3] IR3 was originally built and tested by WSTF in the mid-1980s and has been at KSC ever since.

The key difference between IR3 & IR4 is size. IR4 contains 3,000 pounds of media - ten times the amount in IR3 and theoretically should remove 600 pounds of water. However, flow is done in series from one tower to the next. Therefore, the media in the first tower is going to "take the biggest hit of water removal" compared to the second and third tower. The process is similar to water-purification system where the last vessel in a series is usually used as a "polishing" unit. In effect, IR4 is mole sieving the N_2O_4 nine times more than IR3 does.

Graph 1 indicates molecular sieving effectiveness. Negative values for iron and water-equivalent are good. Negative NO-change is expected with minimizing this value being a primary operational issue.



As of this writing, only three tanker-batches of N_2O_4 have been processed through IR4. Additional runs will indicate further performance capability. The data shows for IR4, the water-equivalent content in the product is reduced by up to 0.10 wt.% and resultant concentration in the product is as low as 0.01 wt.%. As water levels get lower, the near-infrared analysis method required to be adjusted to measure to the lower levels[4]. IR4 does appear to be able to meet the design criteria of reducing the water-equivalent content to less than 0.02 wt.%. Iron levels were reduced by up to 0.12 ppmw and concentration in the final product was as low as 0.02 ppmw, which meets design target of less than 0.05 ppmw. Iron removal seems to be enhanced with IR4 compared to IR3 (0.02 ppmw verses <0.1 ppmw). However, the data circa 1997 & 1998 was predominantly determined via the atomic-absorption method in the Mil-spec with a minimum detection limit around 0.1 ppmw. Later iron analyses were performed using an inductively coupled plasma spectroscopy method with detection limits under 0.01 ppmw. Therefore, it is not apparent if IR4 does a better job of reducing iron content as compared to IR3 or not. From Graph 1, it appears IR3 actually removes more iron, up to 0.4 ppmw, while IR4 only removed up to 0.12 ppmw. Perhaps this is merely a result of the IR3 sources having higher original iron levels than the IR4 sources to date.

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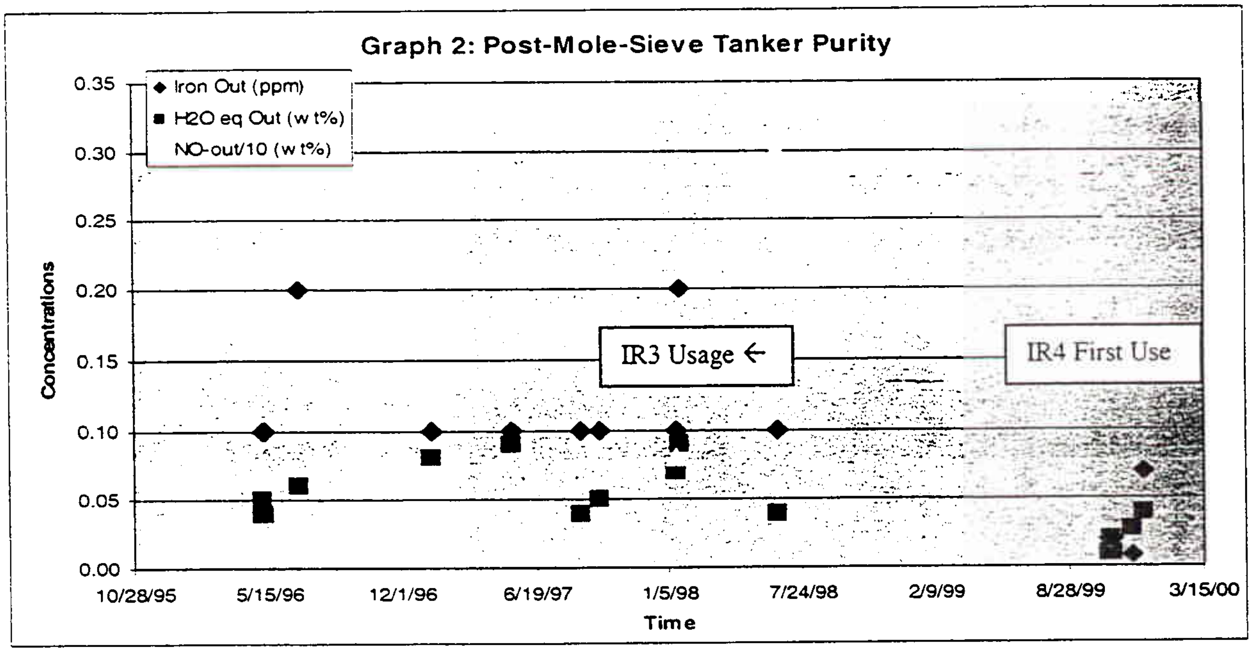
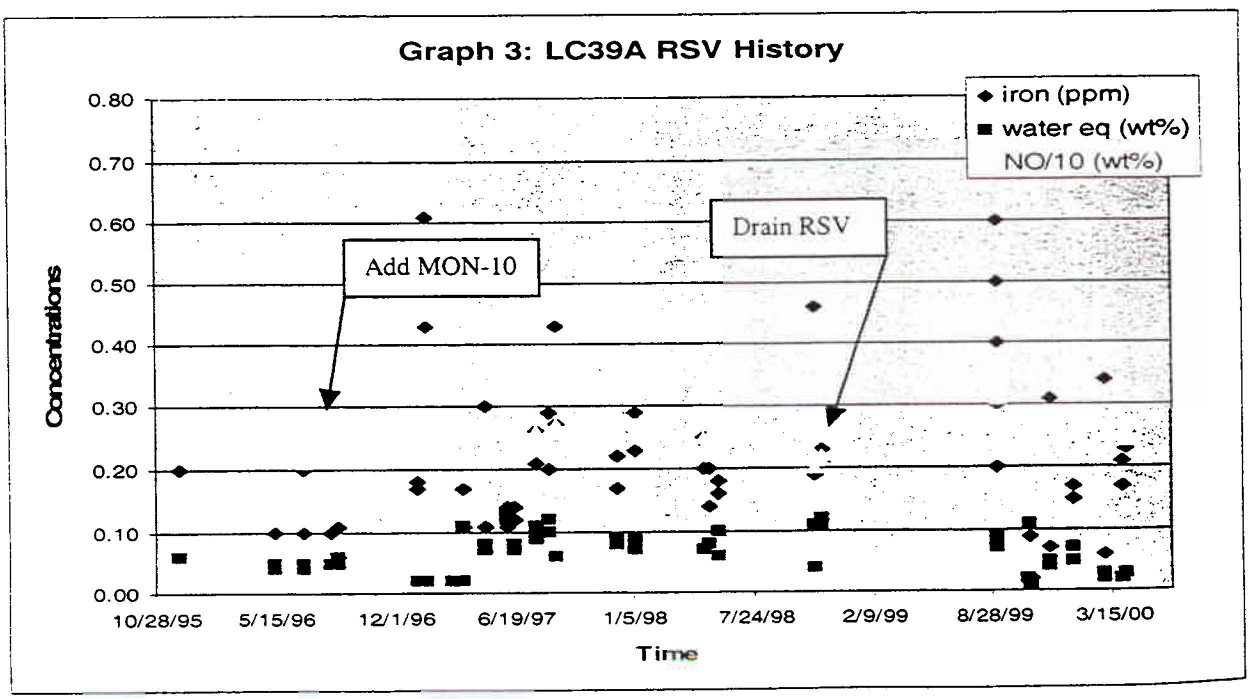
[4] The near infrared method measures the absorbance at 1404 and 1430 nm. The 1404 "peak" is typically very small if at all detectable from the baseline and represents "free water." The 1430 nm peak is actually nitric acid. This peak also became very small in product processed through IR4, requiring adjustments in baseline determinations.

Graph 2 indicates the quality of the N_2O_4 delivered to the two RSVs in the KSC tankers. Note NO levels are 1/10th actual values. Next we will examine the iron, water equivalent, and NO levels of the N_2O_4 stored in the RSVs.

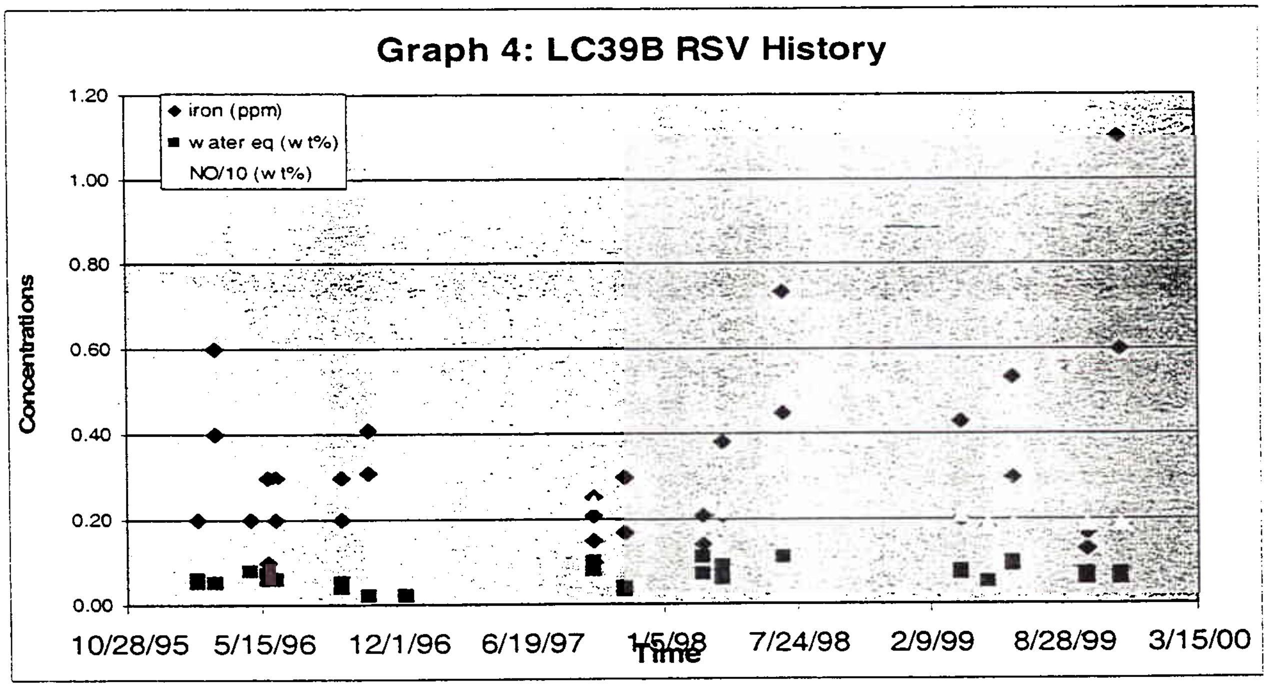


RSV Long Term Purity Results

Tanker loads of molecular-sieved N_2O_4 are delivered to LC39A or B RSVs and off-loaded approximately every-other-mission from either pad. As demonstrated above, the N_2O_4 going into these tanks has generally low iron (<0.1 ppmw), low water equivalent (<0.08 wt.%), and high NO (> 2.5 wt.%) levels. Graphs 3 and 4 each show a four-year history of the two RSVs. Note NO levels are 1/10th actual values.



The LC39A N_2O_4 RSV was replaced in early 1996. After the initial fill, the NO level has remained above 2.0 wt.% but had dropped to this level by January 1999. The water equivalent levels start low but creep up by June 1997 to around 0.10 wt.%. The very low (~0.02 wt.%) water equivalent measurements in early 1997 are suspect due to analytical problems. The large data gap in 1999 is due to pad down time with no launch activities. The RSV was emptied and refilled with the mole-sieved N2O4 (with much higher NO content) from IR4 in October 1999. Since the RSV was refilled in October 1999, the NO level has again declined to 2.5 wt.% during two Shuttle fueling operations. Fortunately, the water equivalent has stayed at a very-low level since the RSV was refilled. Unfortunately, the iron content is all over the place, but does stay under the current SE-S-0073 limit of 1 ppmw.



The LC39B N_2O_4 RSV was replaced in 1994. The two large data gaps represent pad down time for refurbishment with no launch activities. The LC39B N_2O_4 RSV long-term data is dispersed similar to LC39A data and also shows a clear decline in NO levels despite generally 2.5+ wt.% levels from the delivery tankers. The LC39B water equivalent level has remained fairly consistent around 0.10 wt.%. As with LC39A, the LC39B iron level is all over the graph.

Graphs 3 & 4 are admittedly busy but do indicate the variability of the individual analysis results. It was hoped a trend would be evident linking iron, water equivalent, and NO levels. But this is not the case even with four-years of data. To summarize, Table 3 indicates mathematical average iron, NO, and water equivalent results for tankers of N_2O_4 delivered and the LC 39 RSVs (both pads combined) compared to the Tiger Team's proposed limits which would apply to the RSV-to-vehicle interface. Recent data from IR4 and the LC39A RSV do indicate very-low water-equivalent levels are achievable. However, it appears to be very difficult to meet the iron and NO levels in the RSV that were proposed by the Tiger Team.

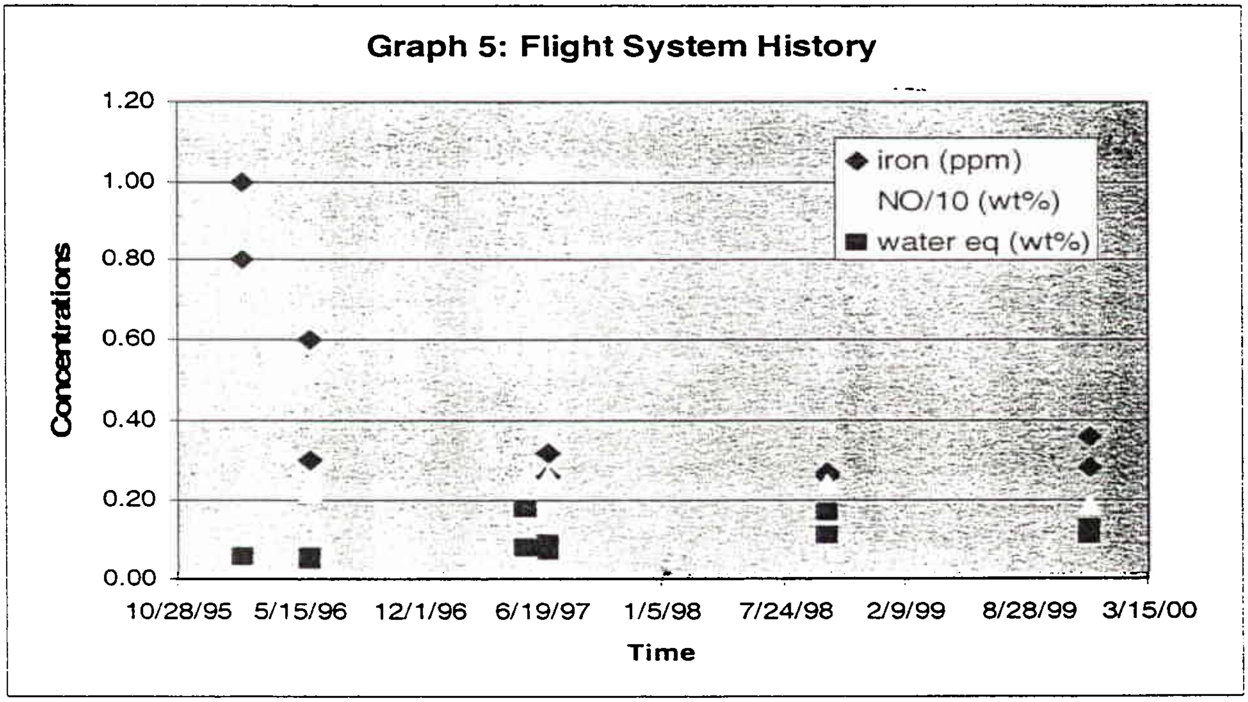
Table 3: Historical Average Values

	Iron Content (ppmw)	NO Content (wt.%)	Water Equivalent (wt.%)
IR3 Ave.	-.1	3.0	0.05
IR4 Ave.	0.02	2.7	0.01
Pad RSV Average	0.32	2.3	0.06
Tiger Team	0.1	2.5	0.05

Iron trends at LC39A and B both show that the Tiger Team's proposed iron limit of 0.1 ppmw could not be achieved. There are several errant iron values above 0.5 ppmw. However, less-than 0.5 ppmw is achieved most of the time. Despite NO levels being above 2.5 wt.% in the delivery tankers, the RSVs are quickly vented to this level and lower by pad operations.

Flight System Long Term Purity Results

The point of reducing initial iron and water-equivalent levels in N_2O_4 is to have these levels carry over into the flight systems where the component failures have occurred. Graph 5 is sample analysis results taken from the Shuttle flight systems during very-limited maintenance activities over the past four years. Samples prior to August 1996 are from flight systems filled prior to the KSC implementing the 3A molecular sieving program.



The NO values fluctuate between 1.9- and 2.6 wt.%. Variable NO-levels are due to many factors. First, the N_2O_4 vendor NO level can vary from 2.5- to 3.0 wt.% in accordance with the procurement specification. Next, system venting operations going from the original delivery tanker, through the molecular sieve, the KSC tanker, the RSV and cross-country piping, and finally into the flight tank reduce NO-levels throughout the process. Obviously, fewer transfers and less system venting should result in generally higher NO-levels. The water-equivalent values generally vary between 0.06- and 0.13 wt.% with an occasional value as high as 0.18 wt.%. The iron levels indicate a downward trend towards the 0.3 ppm-realm during the four years additional molecular sieving has been performed. Unfortunately, this data again suggests the Tiger Teams' proposed iron and water equivalent limits (0.1 ppmw and 0.05 wt.%) might not be met in the flight systems. There have been no flight system failures attributed to iron nitrate since molecular sieving began at KSC until the recent air-half coupling quick-disconnect failure during STS-101 propellant loading operations (early April, 2000).

Conclusions

The new molecular sieve unit, IR4, did meet the design criteria of producing 0.02 wt.% maximum water equivalent and 0.05 ppmw maximum iron content on two-of-three batches of N_2O_4. Due to the short duration of pump running time, an evaluation on the effect on nitric oxide depletion is yet to be conclusively determined. However it appears a loss of 0.1 wt.% should be expected which is consistent with the old unit, IR3. Operating and maintenance activities will be considerably more involved on IR4 than on the old unit, IR3. Additional evaluations will continue on IR4. It has yet to be tested in "circulation mode" with a RSV, a key capability not available with IR3.

Since May 1996, KSC has been processing N_2O_4 through its molecular sieves IR3 and IR4 using the 3A material. Water equivalent and iron content of N_2O_4 delivered into the Space Shuttle RSVs has improved. The higher-purity N_2O_4 does appear to be maintaining most of this higher purity in the RSVs. This improved purity then appears to carry over into the flight hardware as evidenced by the decreased iron and relatively stable water-equivalent levels in Graph 5. As expected, nitric oxide levels do decrease due to system venting as the N_2O_4 moves from one step of the logistics process to the next.

Since there have been fewer failures, molecular sieving and the other Tiger Team activities have apparently produced the net result of decreased RCS N_2O_4 system failures. It is evident the Tiger Teams' proposed N_2O_4 specification changes to lower the water equivalent and iron limits cannot be readily met in the RSVs nor the flight systems. Despite best efforts to deliver "Tiger Team Grade" N_2O_4 to the flight hardware, this purity level is not achieved although it is more pure than it was when KSC molecular sieving started almost four years ago.

N_2O_4 quality in the RSVs and flight systems shall continue to be monitored. RSV NO-conservation measures should be examined to attempt to keep the NO levels more near 2.5 wt.% than the lower values commonly found in the RSVs. Higher NO levels increase iron nitrate solubility in N_2O_4 so it would be less likely to precipitate out of solution and cause system problems. The 3A material molecular sieving operation has become a routine activity at KSC and will continue to support the Shuttle Program. Further data shall be collected to determine if current trends are accurate. IR4 operations and performance shall continue to be monitored and regeneration methods shall be developed.

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